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Industrial Emission Treatment Technologies

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1. Introduction

Industrial emissions are becoming one of the most significant environmental issues facing industries. Gaseous emissions from industrial operations can adversely affect the atmosphere (e.g. carbon dioxide CO_2 , nitrous oxide N_2O , volatile organic compounds VOCs, steam) and health of people living in surrounding neighbourhoods (e.g. odour, particulates, heavy metals).

The burning of fossil fuels and biomass is the most significant source of air pollutants such as sulphur dioxide SO_2 , carbon monoxide CO , nitrogen oxides NO and N_2O (known collectively as NO_x), VOCs and some heavy metals. The main source of SO_2 emission is from the combustion of sulphur-containing fuels. Sulphurs are present in coal in the form of pyrites, sulphates or organic sulphurs. In some deposits, the sulphur content can be as high as 4%. Upon combustion, most of the sulphur is converted to SO_2 , with a small amount being further oxidized to sulphur trioxide SO_3 . In the absence of a catalyst, the formation of SO_3 is slow; over 98% of the combusted sulphur is in the form of SO_2 .

The burning of fossil fuels is also the major anthropogenic source of CO_2 , one of the important greenhouse gases. Coal is the world's most abundant and widely distributed fossil fuel source. Although many alternatives to combustion of coal are being considered, coal will remain as a principal component of the global energy mix for decades. The International Energy Agency expects a 43% increase in its use from 2000 to 2020 (World Nuclear Association, 2011).

Nitrous oxide N_2O with a Global Warming Potential impact factor of 310 CO_2 equivalent is formed as a by-product from the production of adipic and nitric acid, and nitric acid production is currently believed to be the largest industrial source of N_2O emissions contributing to the ozone layer depletion (US EPA, 2010).

Particulate emission is becoming one of the main causes of respiratory disease worldwide. Sources of particulates can be natural or man-made. Some particulates occur naturally, originating from volcanoes, bush fires, dust storms or by human activities such as the burning of fossil fuels in power plants, vehicles, construction and various industrial processes. Increased levels of fine particles in the air affect lung function and in some cases can cause heart disease.

Steam is the most universal energy carrier. Its application is wide spread and it can be found in all aspects of industrial process. Water vapour is the major driver of greenhouse gas-induced climate change (SMH, 2007). The biggest steam user is thermal power stations where steam is used to generate electricity. The steam consumption in a typical thermal power station of 1000MW capacity is about 2,800 t/h which translates to about 800 kg condensate per second (Hoang, 2011). Waste steam can be found in almost every plant/factory where steam is used; from big industrial establishments such as refineries, power plants, chemical factories, steel makers, ore mining, to medium and small plants such as sugar mills and food processing plants.

Odour is also one of the most significant air quality issues facing industry. As the public and regulators are highly sensitive to nuisance odours, the release of any odorous gas/vapour from industry, whether it may or may not represent a health risk, will result in complaints and possibly regulatory fines. Odour is caused by emission of mixtures of chemicals from a wide range of industrial operations, including pulp and paper, chemical manufacturing, refining, mineral processing, paint, plastics, agrichemical manufacturing, sewage treatment, meat works and rendering plants, food processing, and skin and hide processing at tanneries. Prolonged exposure to foul odours usually generates undesirable reactions in the human body such as discomfort, sensory irritation, headaches, respiratory problems, and vomiting.

Stricter environmental regulation in the industrialized countries has triggered the introduction of cleaner technologies in the last decade. The integration of flue gas desulphurisation, low-NO_x, Integrated Gasification Combined Cycle (IGCC), and Pressurised Fluidised Bed Combustion (PFBC) enable coal combustion to occur with higher thermal efficiencies and lower emissions. The combustion of natural gas for electricity generation, transportation and other applications such as industrial boilers has significantly reduced CO₂, SO₂, NO_x and particulate emissions. New carbon capture, storage and sequestration technologies are at the stage of economic feasibility evaluation. Research is focused on deploying large scale demonstration projects that provide a pathway for industry to adopt the technologies at full scale. The three primary separation technologies under research, development and deployment are based on liquid absorption, membranes, and solid adsorption.

In the transport sector, the introduction of catalytic converters, reformulated fuels and the improvement of engine performance have also led to a significant reduction in harmful emissions.

Clean technology research for industrial emission treatment is focussed on technologies that offer the highest efficiencies and lowest emissions. These efforts are directed at research, development and deployment of near zero emission fuel conversion, steam utilisation and recycling, odour reduction technologies as well as the development of renewable energy technologies.

2. Prevention and control of industrial emissions

2.1 Emission control technologies and practices

Various technologies exist that have been designed to remove or treat harmful substances from industrial vent gas. These technologies represent a varying degree of commercial

readiness. Tens of thousands of hours of operation under industrial conditions have been proven for some technologies while others have only recently been demonstrated at commercial plants.

2.1.1 CO₂ control technologies

Post combustion capture (PCC) is a process that separates and captures CO₂ from a large volume of low pressure flue gases. The majority of demonstration projects rely on liquid absorption using a liquid such as ammonia or another amine, although membrane based processes are in demonstration phase, and research toward solid adsorbent technologies is gaining pace. For each of these separation technologies, research is directed towards high performance, efficient materials and processes to achieve cost effective CO₂ capture for the lowest energy penalty. Carbon capture technologies have the potential to dramatically reduce greenhouse gas emissions from coal-fired power stations if they can be deployed as high speed capture technologies with high selectivity and minimal energy loss.

PCC technologies offer flexibility in that they can be retrofitted to existing power plants presenting the opportunity to utilise the massive historical capital investment in existing plants. PCC technologies can also be integrated with new infrastructure, and renewable technologies can be integrated with PCC. In addition, PCC can be used to capture CO₂ from a range of industrial sources.

Liquid absorbents:

In the PCC process, flue gases from the power station are typically cooled then fed into a CO₂ absorber as shown in Figure 1. The process of capturing CO₂ using aqueous amines has been practiced for over 80 years (Rochelle, 2009) in the removal of CO₂ from natural gas and in the production of beverage-grade CO₂. In the process shown in Figure 1, flue gas that contains CO₂ is contacted with an aqueous amine or ammonia or novel solvent in an absorber column at a relatively low temperature. The CO₂ is absorbed by the solvent. The CO₂ loaded solvent is pumped to a stripping column where it is heated to regenerate the solvent and release the CO₂. The hot regenerated solvent is then returned to the absorber column through a heat exchanger, which cools the hot solvent and preheats the CO₂ loaded solvent going to the stripper. This process has some limitations that include solvent loss, corrosion, and the high energy demand for regeneration of the solvent. Indeed, most of the energy required to capture CO₂ is consumed in heating the CO₂ loaded solvent in the stripper column. It is estimated that a 500 MW_e power plant requires on the order of 1000 metric tons of absorbent in order to separate more than 80 per cent of the CO₂ from flue gas (DOE, 2010).

Research and development activities for solvent based PCC technologies include the synthesis and scale up of novel solvents with higher selectivity and capacity, using waste heat to increase solvent capacity and capture rate, improving the chemical and thermal stability of solvents, and new process designs to reduce footprint. Solvent systems that are responsive to physical and chemical switches other than the traditional thermal and pressure swings are also under investigation. One class of novel solvents under investigation is ionic liquids or low temperature molten salts. They are composed of cations and anions and are liquids at ambient conditions. They are non-volatile, hence

avoiding solvent loss, and non-flammable. Their chemical structure can be designed so that they absorb CO_2 and require a low energy for the desorption of CO_2 (Gurkan, 2010; Wang, 2010).

Membranes:

Membrane based separation processes for CO_2 , although a less mature technology than the aqueous amine solvent technology, have some advantages over solvent technologies for separating gases. These advantageous aspects include a simple operation with no moving parts, a technology that builds on existing low-cost technology that is already proven at similar scales in other industries - e.g. desalination, an environmentally benign separation technology without the use of hazardous chemicals, a compact and modular technology with a small footprint, and finally a low energy technology (DOE, 2010; Merkel, 2010). Figure 2 illustrates the small footprint of a membrane based gas separation unit for the removal of CO_2 from natural gas as compared to an amine absorption unit. The amine absorption unit was decommissioned because the columns were corroding over time due to the aggressive nature of the amine solution used to adsorb the CO_2 . The membrane unit is dwarfed by the amine unit, although both technologies are employed to perform the same separation.

Challenges for membrane based separation include particulate matter and its impact on membrane lifetime, and due to the youth of this technology, there is a lack of operating experience in the power industry. Recent demonstration trials of membrane technology by Membrane Technology and Research Inc (MTR) have been completed in collaboration with the Arizona Public Service Cholla power plant for PCC with the process diagram shown in Figure 3.

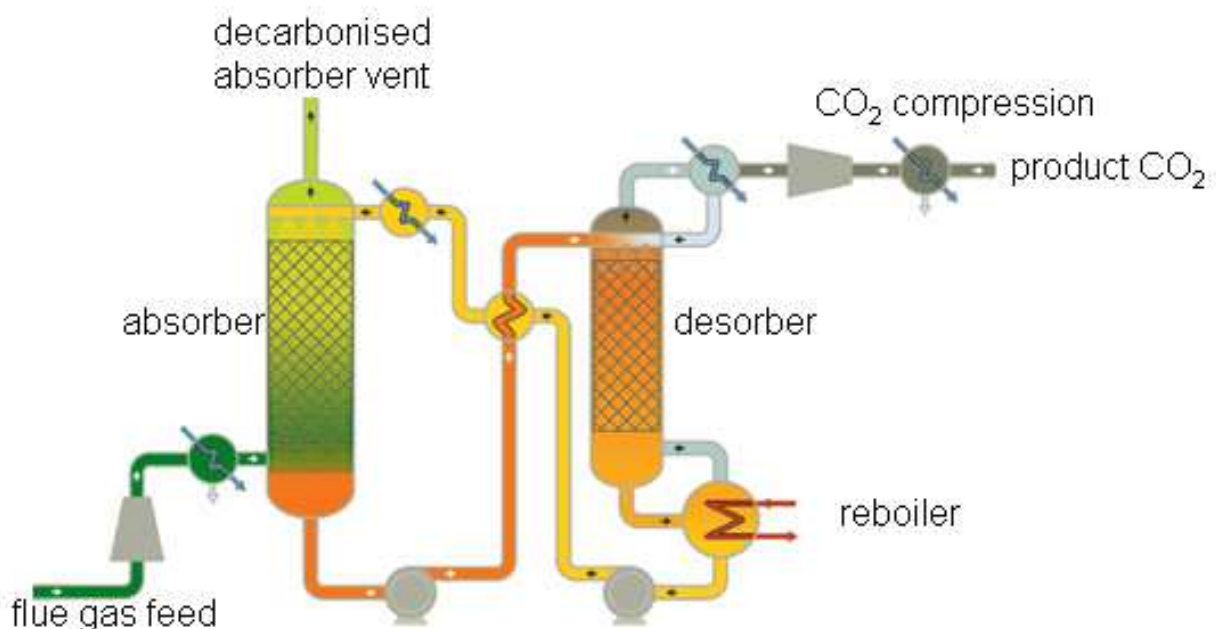


Fig. 1. Solvent based CO_2 capture process flow diagram (adapted from Siemens, 2008).

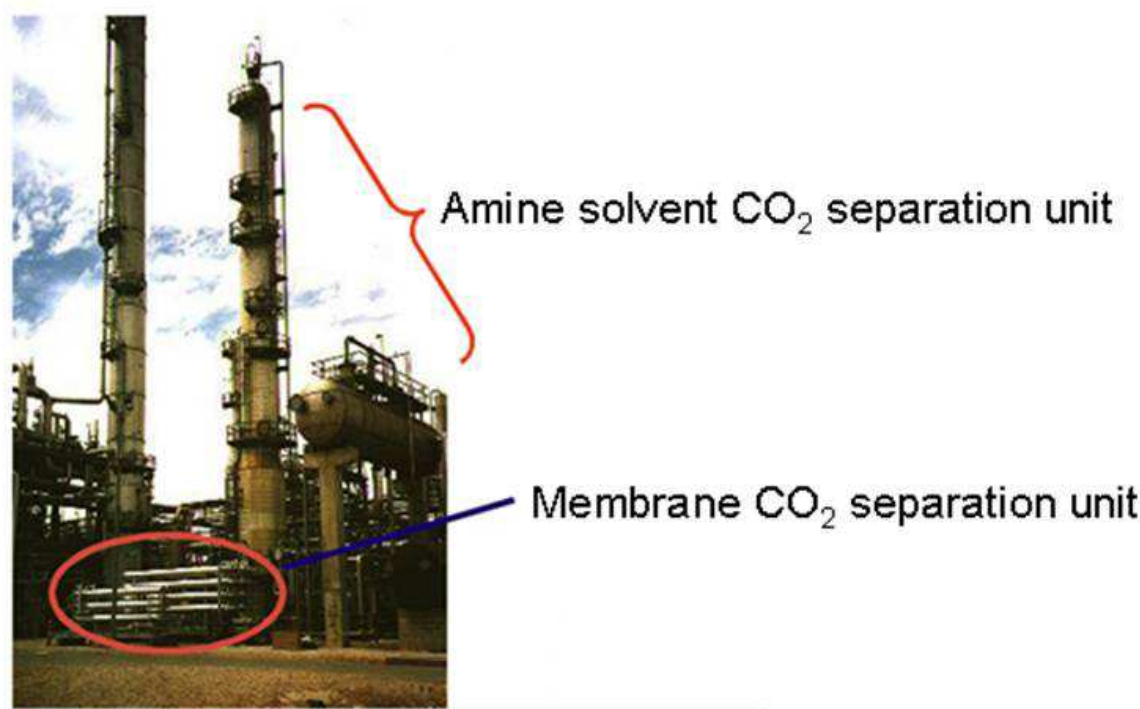


Fig. 2. Comparison of footprint for solvent versus membrane process units for CO₂ separation (adapted from Fleming, 2009).

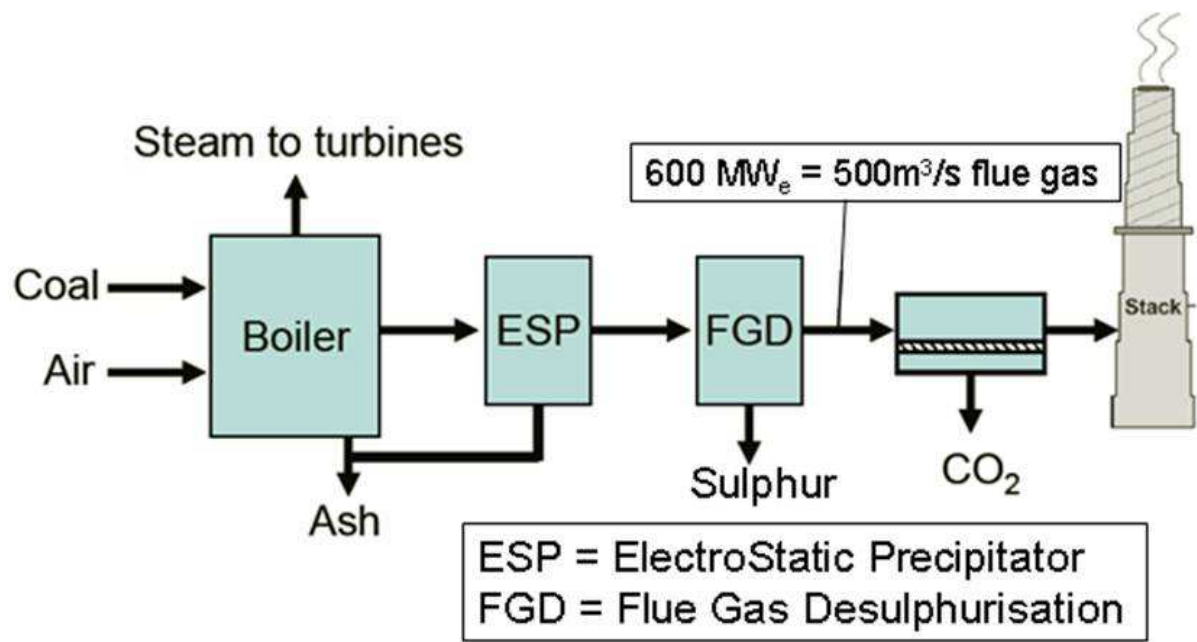


Fig. 3. Membrane based CO₂ capture process flow diagram (adapted from Merkel, 2010).

Performance data for the MTR Polaris™ membrane have been reported for temperatures ranging from 25-50°C (Merkel, 2010). These recent trials have indicated that 95% of the CO₂ from flue gas

can be separated at a parasitic energy penalty of 15% using the Polaris™ membrane technology, which can be compared to the estimated solvent technology parasitic energy penalty of 30% (Merkel, 2010). A parasitic energy penalty is indicative of the additional fuel that must be burned (to enable carbon capture) for the same power output. Current material and process efficiency improvements for both technologies aim toward < 10% parasitic energy penalty.

Membranes made from thermally stable polymers offer attractive features such as dimensional stability at elevated temperature, resistance to oxidation and thermal degradation, and stability to harsh chemical environments. A new membrane based on thermally rearranged (TR) polymers has been reported that can perform CO₂ separation processes at ambient temperatures as well as at operation temperatures as high as 230°C (Park, 2010). The gas transport in these TR polymer membranes occurs through a pore architecture that consists of micropores (<2 nm) that allow fast diffusion of gases connected by ultramicropores (<0.7 nm) that are responsible for the molecular sieving. The method of creating this efficient pore architecture in thermally stable glassy polymers is via thermal rearrangement, hence the name TR polymer membranes. The pore architecture can be tuned for particular gas and vapour separations, hence TR polymer membranes are currently in research and development stage for numerous commercial applications including CO₂ capture.

Solid sorbents:

Solid adsorbents utilized in chemical separation applications include molecular sieves, activated carbons, and zeolites, all of which are porous materials with high surface area, typically up to 3000 m² g⁻¹. Pressure swing adsorption (PSA) is a process that relies on preferential adsorption of the CO₂ from gas mixtures when exposed to the porous materials at a high pressure. The pressure is subsequently reduced and the CO₂ is desorbed from the porous solid. PSA technology has relatively low energy requirements and capital costs. Much current research focuses on the development of regenerable solid adsorbents with chemical structures and pore architectures that are designed to increase the selectivity and adsorption capacity for CO₂ and lower the energy consumption in the sorption-desorption cycle. Similar to the research directions in solvent absorption, solid adsorbent materials that are responsive to physical and chemical switches other than thermal or pressure swings, e.g. electrical, magnetic, mechanical, or light stimulation, or the presence of particular chemical species to facilitate either uptake or release of CO₂ are also under investigation.

Metal organic frameworks (MOFs) are one of the topics of current research focus. MOFs are materials with extremely high surface areas, up to 10,000 m²g⁻¹, and their chemistry can be tailored to control the porosity and capacity for CO₂. They are synthesized using metal atoms or clusters linked in a periodic fashion via organic linker molecules to form crystalline porous structures. Figure 4 illustrates the pore architecture of a class of MOF that uses imidazolate organic linkers to achieve a pore architecture that resembles an hourglass with large cages separated by a constriction which results from the asymmetric connectivity of the imidazolate ring (Thornton, 2011). These frameworks are known as zeolitic imidazolate frameworks (ZIFs) and they have been shown through modelling and experiment to offer great promise for CO₂ separations (DOE, 2010). Another characteristic of the best performing candidate CO₂ adsorbent MOFs is that they possess a high density of accessible open metal sites (Yazaydın, 2009). Combining the ability to tailor chemistry in order to tune the affinity for a particular gas, along with the ability to architecture the porosity of membranes and solid adsorbents, is an area of much current research.

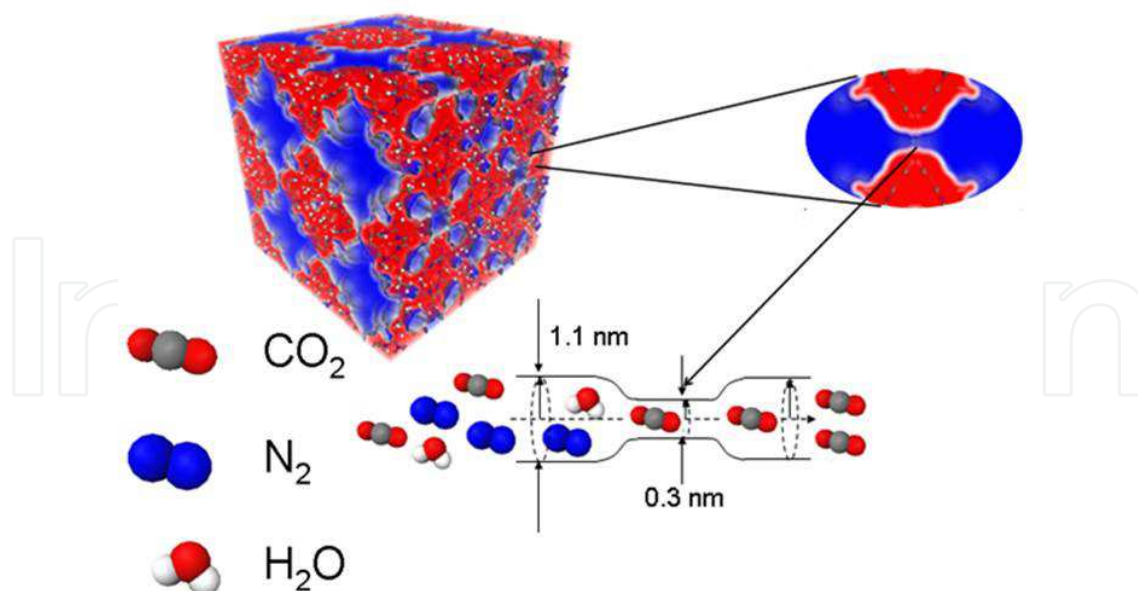


Fig. 4. Schematic pore architecture of a class of MOF known as zeolitic imidazolate frameworks (ZIFs) illustrating the hourglass shaped porosity in which the larger cages provide efficient access for gas molecules to the selective constrictions (adapted from Thornton, 2011).

2.1.2 NO_x control technologies for nitric acid plants

Nitrous oxide (N_2O) is a by-product of the manufacture of nitric acid by the Ostwald process. This process involves three basic operations: (i) the combustion of ammonia into nitric oxide, (ii) the oxidation of nitric oxide into nitrogen dioxide and (iii) the absorption of nitrogen dioxide in water to produce nitric acid (Perez-Ramirez, 2003; Maurer, 2005).

Depending the location in the process, the approaches of lowering N_2O from nitric acid plants can be classified into three groups:

- Primary: preventing N_2O being formed in the ammonia burner
- Secondary: removal of N_2O from NO_x gases between the ammonia converter and the absorption column.
- Tertiary: removal of N_2O from the tail gas downstream.

The development of N_2O abatement systems aims at the achievement of high efficiency (>90% N_2O conversion) and selectivity (<0.2% NO loss) (Perez-Ramirez, 2003).

Technologies for primary abatement:

The catalytic oxidation of ammonia over platinum-rhodium gauzes takes place through several reaction paths depending on the temperature. Under current industrial operating conditions, the process yields up to 97% NO, the desired product in nitric acid production. Although the process is well established, there are still research efforts in improving the selectivity not only for production yield but also for lowering N_2O emission. Thus optimising the NO selectivity by improving the catalyst, reactor design and operating conditions are considered as part of primary abatement. Examples of efforts toward optimisation include changes in the geometry and configurations of gauzes as well as the development of oxide-based catalysts (Groves, 2006; Perez-Ramirez, 2004a; Perez-Ramirez, 2006a).

Technologies for secondary abatement:

Thermal decomposition:

Norsk Hydro developed a reactor technology based on the thermal gas phase decomposition occurring down-stream from the reactor chamber. The technology has been implemented in an acid plant in Porsgumn Norway in 1990 (Perez-Ramirez, 2004b).

Catalytic decomposition:

Nitrous oxide emissions from nitric acid production are influenced by the degree to which emission control efforts are applied in both new and existing plants (Mainhardt, 1996). The catalytic reduction of N_2O is well known from the open and patent literatures. It was reported that N_2O can be decomposed into N_2 and O_2 over various types of noble metal, metal oxide and mixed oxide catalysts. However there are a limited number of catalysts that have been commercialised. An ideal industrial catalyst must satisfy the N_2O reduction target of >90% under severe oxidising environments at high temperature and pressure and with a minimal loss of NO.

Norsk Hydro patented a series of catalysts comprising $Co_{3-x}M_xO_4$ where $M=Fe$ or Al and $x=0$ to 2 supported on CeO_2 . The presence of a small amount of ZrO_2 was reported to prevent the degradation of catalyst activity (Nirisen, 2002, 2004). This catalyst is claimed to be non-NO destructive, versatile, active and thermally stable, which can be applied over a wide temperature and gas composition range, e.g. in the presence of oxygen and water vapour. Based on this invention, Norsk Hydro successfully commercialised the catalysts NH-1 and its second generation NH-2.

A Cu-Zn-Al catalyst was developed, patented and commercialised by BASF in 1999 (Schumacher, 1999, 2004). The best catalyst composition was reported as 8% wt CuO, 30% wt ZnO and 62% Al_2O_3 . The catalyst was fabricated in star extruded form denoted as O3-80, O3-85 and O3-86.

A Ce-Co catalyst was commercialised by Yara International as Yara 58-Y1. It contains >80% cerium oxide, <1% cobalt (II, III) oxide and <1% aluminium cobalt tetraoxide (MSDS, 2008). This Yara catalyst is claimed to be able to achieve greater than 90% N_2O conversion. This N_2O abatement catalyst technology has been tested and installed in many industrial locations, including 11 Yara plants and 11 locations under the clean development mechanism (CDM) or joint implementation (JI) countries as defined by the Kyoto Protocol (Matthey, 2008).

Johnson Matthey, Yara, Mitsui, Alloy Engineering, Födisch AG, and N.serve have formed a globally alliance called N.serve-Johnson Matthey Alliance in 2008. The N.serve-Johnson Matthey Alliance technology is based on the Yara secondary N_2O abatement catalyst, Yara 58-Y1 and Amoxis® type 10-1R, a lanthanum-cerium perovskite catalyst.

Hermisdorfer Institut Für Technische Keramik (HITK) has patented and produced a ceramic based catalyst consisting of metal oxides such as Cr, Mn, Fe, Co, Ni, Cu and La on a porous ceramic support (Burckhardt, 2000). The patent claims that at temperature above 800°C, 100% N_2O conversion is achievable in laboratory and pilot plant tests.

Apart from the above significant developments, there are a number of catalyst inventions available from the patent literature (Vernooy, 2002a, 2002b; Neveu, 1999; Hamon, 2004; Schwefer, 2001a; Jantsch, 2009; Neumann, 2007; Axon, 2004; Paul, 1978).

Technologies for tertiary abatement:

The tail-gas, leaving the absorber column, contains N₂O, NO_x, O₂ and H₂O at temperatures from 523-773K at pressures of 3-13 bar (Perez-Ramirez, 2003).

The composition of the gas at the outlet of the absorber during stable operation varies depending on industrial operation conditions as shown in Table 1 (Perez-Ramirez, 2003).

| Gas | Concentration | Typical value |
|--------------------------|---------------|---------------|
| NO _x (ppm) | 100–3500 | 200 |
| N ₂ O (ppm) | 300–3500 | 1500 |
| O ₂ (vol.%) | 1–4 | 2.5 |
| H ₂ O (vol.%) | 0.3–2 | 0.5 |

Table 1. Composition of the tail-gas at the outlet of the N₂O absorber (balanced by N₂) for a nitric acid plant of 1500 t HNO₃ per day and a tail-gas flow of 200,000Nm³ h⁻¹.

Major developers/suppliers for tertiary abatement catalysts are Krupp Uhde, ECN/CRI , Yara International, Du Pont, University Jagiellonski, Institute NawozÓw Sztucznych, N.E. Chemcat. Uhde has developed and commercialised a system for the removal of N₂O and NO_x from the tail gas of nitric acid plants under the trade name EnviNO_x®. The system features a tail gas reactor consisting of an iron zeolite catalyst installed directly upstream of the tail gas turbine. The EnviNO_x® catalysts are manufactured by Süd-Chemie with brand names EnviCat®-N₂O and EnviCat®-NO_x.

The Uhde EnviNO_x® process was first implemented in 2003 in a 1000 Mtpd dual-pressure nitric acid plant by AMI in Linz (Austria). The tail-gas temperature is about 437°C and the applied configuration consisted of a single reactor with two beds of iron-zeolite with intermediate ammonia injection. The presence of nitric oxide in the inlet gas is vital to promote the N₂O decomposition. The reactor in the AMI plant is reported to operate at a stable N₂O conversion of 98% (Hevia, 2008).

The Energy Research Center of the Netherlands (ECN) has developed a combined catalytic technology for the removal of NO_x and N₂O based on selective catalytic reduction (SCR) using propane as a reducing agent in 2003. Iron and cobalt-containing zeolites are placed in series in a single reactor operated at pressure up to 10 bar. The conversions of N₂O and NO_x ~ 90% were achieved; however, the economic evaluation indicated no cost advantage due to the high dosing of propane (Schwefer, 2001b).

In 2006, ECN tested a trimetallic zeolite-based ECN catalyst prepared by CRI at a pilot scale in a side stream of a nitric acid plant in Ijmuiden, the Netherlands. This N₂O decomposition process has been commercialised in 2007 (Brink, 2002). This catalyst requires no addition of a reducing agent. It can be operated at temperatures of 475-525°C and at pressures of 1-12 bar, with N₂O conversions of 70-95%.

Yara patented a novel ex-framework FeZSM-5 catalyst that led to remarkable performance in simulated tail gases compared to FeZSM-5 catalysts prepared by ion exchange. The multimetallic zeolite and Fe catalyst is used in direct catalytic N₂O decomposition (Perez-Ramirez, 2004b, 2006b).

N.E. Chemcat has developed and commercialised a catalyst named DASH-30D D812. The catalyst consists of palladium supported on alumina silica and magnesium oxide. The catalyst has been installed in numbers of commercial plants by N.E. Chemcat and Sumitomo Engineering including the Caprolactam production plant in Thailand in 2008 (TEI, 2009; CDM 2002), the Pakarab Fertilizer plant in Multan, Pakistan, 2007 (CDM, 2002), the nitric acid plant of the Kaifeng Jinkai Chemical Ind. Co., Ltd, China, 2007 (CDM, 2006a) and the nitric acid plant of Liuzhou Chemical Industry Co., Ltd, China, 2009 (CDM, 2006b). Apart from the above significant developments, there are number of catalyst inventions available from the patent literatures (Russo, 2007).

NO_x control technologies for combustion processes:

In combustion processes NO_x is formed by the oxidation of fuels that have high nitrogen content such as coal and residual oils. Combustion of low nitrogen content fuels such as distillates or natural gas also produce NO_x but in lesser amounts. The most common NO_x control technology for the combustion process is low-NO_x burners (LNB). They can be used separately or in combination with post-combustion control technologies such as selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR). This technology involves the modification of the process into a two stage combustion process: a fuel-rich zone where primary combustion takes place and a fuel-lean zone for secondary combustion at lower temperature. LNB technology affords up to 60% reduction for the combustion process (Watts, 2000).

Selective non-catalytic reduction (SNCR) is based on the chemical reduction of NO_x molecules into molecular nitrogen (N₂) and water vapour (H₂O) by a nitrogen-based reducing agent such as ammonia or urea. In this process the reducing agent is injected into the post-combustion flue gas stream and heat from the boiler provides the energy for the reduction reaction.

Like SNCR, the selective catalytic reduction (SCR) is based on the reduction of NO_x by a reducing reagent except that it is catalysed by a solid catalyst. In this process, a solid catalyst bed is installed downstream of the combustion chamber and ammonia is used as a reducing agent. NO_x reductions up to 90% can be achieved by optimising the reactor design and operation such as ammonia dosage and mixing (Hesser, 2005).

2.1.3 SO₂ control technologies

Flue gas desulphurisation:

SO₂ emission is known to have detrimental effects on human health and the environment. SO_x emissions are directly linked to the initial sulfur content of the fuel and the combustion parameters do not influence the amount of SO_x emitted. To meet emissions regulations, especially when burning high-sulphur coals, it is essential to achieve high levels of SO₂ removal, usually 90% or higher.

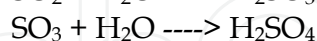
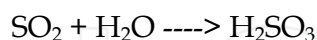
The most widely used technology for SO₂ emission control is the flue gas desulphurisation (FGD) process. An extensive review of this technology can be found in the Technical Status Report 012 Cleaner Coal Technology Programme (Kamall, 2000).

FGD technologies can be grouped into wet, dry and regenerable FGD. In wet FGD processes flue gas contacts an alkaline slurry in the absorber. The absorber may take various forms (spray tower or tray tower), depending on the manufacturer and desired process

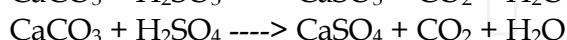
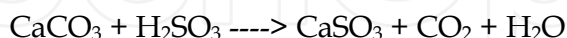
configuration. However, the most often used absorber application is the counterflow vertically oriented spray tower (Kamall, 2000; Srivastava, 2000; Faustine, 2008).

The major reactions occurring in wet FGD are:

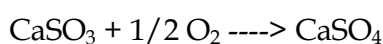
i. Absorption



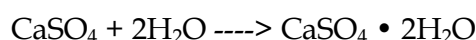
ii. Neutralization



iii. Oxidation



iv. Crystallization



A relatively high degree of SO_2 removal is usually achieved, with a high level of sorbent utilization. The wet FGD technology has been significantly improved since its first introduction to industry in the 1970s. The new technology features state-of-the-art designs and materials of construction. Highly efficient, compact, and less expensive technology with minimal waste disposal problems has been developed by incorporating oxidation of the calcium sulphite sludge into wallboard-grade gypsum. In addition, wet FGD systems can remove significant particulates due to the contact between gas and liquid phases.

In wet FGD, the limestone forced oxidation (LSFO) is most widely used. In LSFO, air is added to the reaction tank to oxidise the spent slurry to gypsum. The gypsum is removed from the reaction tank prior to the slurry being recycled to the absorber.

In the dry FGD process, SO_2 -containing flue gas contacts a lime sorbent. The sorbent can be delivered to flue gas in an aqueous slurry form or as a dry powder. Both methods require dedicated absorber vessels in order for the sorbent to react with SO_2 . By-product solids are collected in a dry form along with fly ash from the boiler in the existing particulate removal equipment. Compared with wet FGD systems, SO_2 removal efficiency and sorbent utilization are usually lower. A typical technology of dry FGD is the lime spray dryer (LSD) technology, a dry scrubbing process generally used for low-sulphur coal (Kamall, 2000; Srivastava, 2000; Faustine, 2008).

Hydrodesulphurisation:

The principal operation of a refinery is to convert crude oil into products such as LPG, gasoline, kerosene, diesel, lubricants and feedstocks for petrochemical industries. After separation of the crude oil into different fractions by conventional distillation, these streams are transformed into products with high values by a variety of catalytic processes such as hydrogenation, isomerization, aromatization, alkylation, cracking and hydrotreating. Hydrodesulphurisation (HDS) is a catalytic hydrotreating process. It is applied to remove sulphur from natural gas and from refined petroleum products.

The primary objective of refiners before 1990 was to maximise the conversion of heavy oils into gasoline and middle distillates. In the refining processes, the purpose of removing sulphur is to protect the noble metal catalyst from poisoning. The restriction in harmful substance emissions to the atmosphere has spurred the focus on the production of cleaner products. Significant capital investments in the refining industries are necessary to produce cleaner middle distillates to meet environmental standards. Thus another important reason for removing sulphur is to eliminate the SO_2 emission that results from burning refinery products. In a typical industrial hydrodesulphurisation unit, the hydrodesulphurization reaction takes place in a fixed-bed reactor at elevated temperature, 300 to 400°C, and at pressures from 30 to 130atm (CEP, 2009). Industrial catalysts for this purpose consist of cobalt-molybdenum or nickel-molybdenum supported on alumina.

2.1.4 Particulate control technologies

A variety of particulate removal technologies, with different physical and economic characteristics are available.

Electrostatic precipitator (ESP):

This process removes particles by using an electrostatic field to attract the particles onto the electrodes (Rankin, 2011). Once the particles are collected, they are removed through a hopper. ESPs are especially efficient in collecting fine particulates and can also capture trace emissions of some toxic metals with an efficiency of 99% (World Bank Group, 1998). They can operate at elevated temperatures with a very low pressure drop. ESPs have been used in numerous industries such as alumina refineries and cement production plants.

Filters and dust collectors:

Baghouses collect dust by passing flue gases through a fabric that acts as a filter. Depending on the application, various types of filter media including woven fabric, plastic, ceramic, and metallic are commercially available. The flue gas temperature determines the operating temperature of the baghouse gas and the choice of fabric. Fabric filters are efficient (99.9% removal) for both high and low concentrations of particles but are suitable only for dry and free-flowing particles.

Wet scrubbers:

This process relies on the removal of dust particles from a gas stream by liquid phase. A wet-scrubbing technology is used where particulates cannot be removed easily in a dry form; however, the technology generates an effluent that needs to be treated.

2.1.5 Odour control technologies

Odour problems are complex issues, and finding a suitable odour control technique is a challenge as there are numerous options available including physical, chemical and biological treatments. Typical industrial odour emissions are shown in Table 2. High process efficiencies are required for a number of reasons but mainly because humans are very sensitive to low concentrations of odorous substances. The odour thresholds of some substances are shown in Table 3.

| Industry | Odorous compounds emitted |
|--------------------------------|--|
| Pulp & paper | H ₂ S, mercaptans, DMS, DMDS |
| Petroleum | Mercaptans, phenolic compounds, aldehydes |
| Iron & Steel manufacture | H ₂ S |
| Oil & Gas extraction | H ₂ S, other reduced sulphur compounds |
| Waste water treatment plants | H ₂ S, NH ₃ |
| Chemical | H ₂ S, mercaptans, phenols, ammonia, organics |
| Tannery | Reduced sulphides |
| Solid Waste Landfill sites | H ₂ S, decaying organics |
| Organic fertilisers production | Reduced sulphides, amines |

Table 2. Typical industrial odour emissions.

| Compound | Odour Detection Threshold (ppm) | Odour Type |
|---------------------|---------------------------------|------------------------|
| Hydrogen sulphide | 0.0005 | Rotten egg |
| Mercaptans | 0.0001-0.001 | Garlic, rotten cabbage |
| Dimethyl sulphide | 0.001 | Decayed cabbage |
| Dimethyl disulphide | 0.16-25 | Decayed organic matter |
| Ammonia | 55 | |
| Trimethylamine | 0.00021 | Rotten fish |
| Methyl amine | 0.021 | Fishy |

Table 3. Detection thresholds for various odorous compounds.

There is a number of available technologies but their applicability is dependant on the characteristics and the physical and chemical properties of the vent gas (Schleglmich, 2005; Busca, 2003).

Wet scrubbing removes odorous compounds by effectively dissolving the vent gas in an aqueous solution. This method can be extremely effective but may transfer the problem from air to waste water.

Adsorption of odorous compounds onto materials with a large surface (eg. activated carbon) offers one of the lowest capital costs. The adsorption media has to be replaced or regenerated based on the amount of odorous compounds removed. As with wet scrubbing, regeneration of adsorbent with steam may transfer the problem from air to waste water. Another problem with adsorption is that the vented gas needs to be free of oil and water as this may clog pores thus reduce the effectiveness of odour removal.

Biofiltration involves passing the odorous gas through a bed of material (e.g. soil, bark, organic mater, synthetic packing). The odorous compounds are adsorbed onto the surface of the bed of material and are then subsequently broken down by microbial action. Biofiltration is suitable for large gas flow rates, and it has low operating costs, but it requires a very large foot print.

Thermal oxidation, at temperatures up to 800°C, of odorous compounds can be very effective but the capital and operating costs are high. Additional air quality problems may arise from the combustion products such as SO_x and NO_x (Busca, 2003).

Catalytic oxidation of odorous gas offers significant advantages over thermal oxidation, by either speeding up the oxidation reaction or by lowering the required reaction temperature (Busca, 2003; Kahn, 2000). The Commonwealth Scientific & Industrial Research Organisation (CSIRO) has developed versatile catalysts that have been tested and found effective at removing odorous compounds from vapour streams (O'Neill, 2005). These catalysts operate at very low temperature, between 100-300°C, providing significant operational savings and a reduced carbon footprint. The technology is very versatile, it can accommodate very low to high gas flowrates. This technology can be extended to various industrial operations including food processing and preparation, pulp & paper manufacturing, petrochemical industries, chemical manufacturing, cement manufacturing, minerals processing and waste water treatment. The technology is being commercialised by Catalytic Solutions International (CSI) Pty Ltd, based in Perth Western Australia (Figure 5).



Fig. 5. Catalytic pilot reactor at final completion (Catalytic Solutions International Pty Ltd – Australia, 2011).

2.1.6 Industrial steam emission control technologies

Steam is almost exclusively produced in boilers, the efficiency of which is about 70-80%. Steam is also generated as a by-product of processes such as an evaporator, or when water is used as the cooling medium. Steam generation is an energy intensive process. Fuel cost is the main component in the cost of steam production. Other factors such as the water inlet temperature and the pressure and temperature of the product steam also affect the cost of steam generation (CADDET Energy Efficiency, 2001).

In an industrial process, after transferring its energy, the pressure and temperature of the steam drop significantly. During the process, it is contaminated with volatile chemicals and gases such as air and carbon dioxide. A common practice to deal with spent steam is to use a condenser to collect the water or to discharge the steam to the atmosphere. Discharging the

spent steam to atmosphere is not only an energy loss — it is at the same time an environmental issue.

With a higher energy cost and a growing concern regarding environmental effects, it is highly desirable to recover the energy loss by recycling the spent steam. The first step in this process is to remove or separate the steam from other gaseous and volatile impurities.

The energy recovery from waste steam can be partially accomplished by using a heat exchanger for multi-effect evaporation when possible or by a vapour recompression process to make the steam usable for other purposes. For example, in addition to the recommendation of using feedwater economisers for waste heat recovery (Steam Tip Sheet 3, 2006), the US DOE has considered the following approaches to waste steam recovery (Steam Tip Sheet 13, 14, 29, 2006):

- Send low-grade waste steam to power absorption chillers.
- Use steam jet ejectors or thermocompressors to reduce venting of low pressure steam.
- Use vapour recompression to recover low pressure waste steam.
- Use a vent condenser to recover flash steam energy.

Vapour recompression appears to be the most advanced technique. It is comprised of (i) thermal vapour recompression and (ii) mechanical vapour compression, with mechanical vapour compression being the favoured option. Limitations of the current recompression techniques include:

- Additional energy is needed to boost the waste steam to higher potential.
- They cannot handle “dirty” steam, i.e. steam containing impurities. The presence of air, especially at higher volume concentrations, can affect the operation of the vapour recompression process. The reprocessed steam still contains gases and impurities as the process cannot eliminate them.

Industrial interest has stimulated numerous investigations into methods of separating and recovering spent steam for both economical and environmental benefits.

Membranes are commonly used in the steam reforming process, where hydrogen is separated from the exit gas mixture using hydrogen selective membranes. In this process, as well as in the fuel cell context, although the membrane is in contact with the steam, it is not used for steam separation.

RASIRC reported a range of steam processing products based on Nafion™ membrane (Spiegelman, 2009), for example:

- Steam generating units where the function of the membrane is to purify the steam to a level suitable for semiconductor industry or other special applications.
- Gas drying units where water vapour is removed from a gas stream.
- Humidity controlled units where water vapour is introduced into a gas stream using membranes.

A Hewlett-Packard patent (Hewlett-Packard, 1989) “Water vapour permeable material for drying gases” reports a method of drying a gas stream using a membrane comprised of a fluoro-carbon polymer containing lithium sulphonate groups. The polymer is reported to be stable under steam conditions.

CSIRO has patented a membrane and process for steam separation and recovery based on a hydrophilic membrane system (CSIRO, 2011a). The technology has been demonstrated at pilot scale.

2.2 Advanced technology developments

Industrialisation offers benefits but also creates pollution. Industrial and environmental sustainability requires new technologies for clean, renewable energy, renewable feed-stocks, cleaner production, and water and air management. Due to society and business awakening, as well as government incentive schemes, new technologies are being developed that embody engineering, economic and environmental considerations.

2.2.1 Materials for industrial emission control

Energy use and emissions:

Generating power close to where it is needed, or managing when and how energy is delivered and used, can improve energy efficiency, minimise energy consumption, and reduce peak demand on the electricity grid. Energy efficiency improvements proportionally reduce industrial emissions.

There have been significant research and development investments in:

- Materials and processes for lower energy water filtration and desalination.
- New methods to generate oxygen with lower power requirements.
- New methods for producing oxygen at large scales required for power production and leaner combustion processes.
- Greener manufacturing and energy production processes with materials that produce less air and water pollution, and capture pollution before it reaches our atmosphere.
- Efficient fuel combustion in both industry and transport sectors
- Low energy processes for capturing CO₂

The availability of appropriate materials is often critical to the success of new engineering, technology, or processing activities. There will be significant energy saving opportunities through improved materials in reaction unit operations, coupling reactions and separations into hybrid unit operations e.g. syngas separation; hydrogen, carbon monoxide, and carbon dioxide separations, a more economical separation for oxygen enabled combustion, and the use of membrane based separation in place of thermal distillation.

The separation of light olefins from respective saturated hydrocarbons on a commercial scale is performed almost exclusively by cryogenic distillation. This technology is highly energy intensive and there is a strong economic incentive to explore alternative separation technologies.

Catalysis is a critical component of a modern industrialised economy. Catalytic processes are responsible for as much as 90% of chemical production processes (Scott, 1999). Catalysis is currently playing a major role in pollution abatement and prevention, leading to significant industrial waste reduction. During the last decade, significant improvements have been made in energy efficiency for chemical and petrochemical processes, and catalysts have played a major role in these improvements. Cleaner technologies directly address the

cause of emissions during the production process by using higher selective catalysts or by the development of new catalysts to enable the replacement of environmentally harmful inputs. Due to the ready availability of n-butane as a natural gas liquid, together with the imposition of strict pollution control measures on atmospheric benzene emission, the replacement of benzene by n-butane as a feedstock for maleic anhydride has been commercialised using a vanadium phosphorous mixed oxide catalyst.

In the membrane development area, most current research and development focuses on new membrane materials; however, research and development efforts are also directed at controlling specific process conditions and process stream compositions in order to take advantage of existing membrane materials, for example the use of membranes to overcome thermodynamic limitations like azeotropes.

Membranes are selective either by pore size or by their affinity for the permeating components. The intrinsic performance characteristics of a membrane material are its selectivity and flux. These characteristics are controlled by the membrane material composition, surface structure and morphology and its compatibility to industrial process operations including the nature and chemical composition of the process stream. Large amounts of research have been devoted to gas separations in recent years such as the separation of hydrogen and hydrocarbons in gas recovery unit operations and high-temperature air separation via ceramic membranes with applications in fuel cells and oxygen-rich combustions. Advanced air separation techniques are constantly being re-engineered with primary aims at raising overall operating efficiencies and increasing the production capacity (EPB, 2009). In numerous industries significant energy savings could be achieved if existing air-fueled combustions could be replaced by oxygen-fueled ones. For this to occur, new energy efficient O₂/N₂ separation technologies need to be developed.

Modern transportation is an essential part of our lives. Forefront materials research has offered significant advantages for this sector by:

- improving fuel combustion efficiency,
- introduction of hybrid vehicles, renewable fuels,
- improving fuel cell-powered vehicle performance,
- hydrogen storage, and
- biofuel production.

One current area of research focus for storage materials for future transportation fuels, such as hydrogen and methane, includes the metal organic frameworks (MOFs) discussed earlier in section 2.1.1. Several MOFs have been commercialized by Sigma-Aldrich and manufactured by BASF (Jacoby, 2008). MOFs suitable for hydrogen storage are being developed for use in fuel-cell-powered automobiles. Optimising the pore architecture, heat of adsorption, the gravimetric capacity, and operational stability of the MOFs are all key criteria for translation of this technology from the laboratory to pilot scale and finally deployment (Sumida, 2009).

2.2.2 Clean and renewable energies

Clean and renewable energies are parts of a long term plan to reshape our economy. Materials have played a major role in:

- Solar power
- Wind power
- Hydrogen production solar power
- Biofuels
- Fuels from lignocelluloses, organic wastes
- Energy from waste steams at higher temperatures and pressures

There has been significant growth in photovoltaics (PV) over the past decade and the cost of electricity from this technology continues to decrease. The increased efficiency has been achieved primarily from advances in material development. However there are still materials research and development challenges for PV technologies including the need to continue to increase solar cell efficiency by improving material properties and cell designs. This increase can be achieved by identifying or developing alternate materials e.g. organic photovoltaics (CSIRO, 2011b) and developing novel nanoscale surfaces to increase capture of the full spectrum of sunlight.

Advanced materials and process research, development, and deployment are contributing to today's energy technologies as well as helping to meet the challenges of future energy needs.

3. Conclusion

All industries are moving toward more efficient and low or zero emission processes due to economic benefit, regulation, and concern for health and the environment. New materials and process technologies are playing an increasing role in emission treatment and by-product utilisation. This chapter has focussed on technologies that offer the highest efficiencies and lowest emissions including physical and chemical mechanisms for near-zero emission fuel conversion and industrial commodity production such as cement or via refinery operation, steam utilisation and recycling, and odour reduction. Candidate technologies covered in this chapter include selective catalytic reduction techniques and chemical separation technologies such as absorption, membrane and adsorption based processes. Several research topics were identified for focus, ranging from fundamental modelling and theory linked to rapid screening and optimisation to speed material and process development through to process conditions suitable for scale-up and deployment. Low energy, efficient, reliable, and environmentally benign emission treatment technologies are one goal of modern process scientists and engineers, with the future holding the promise of closed loop production.

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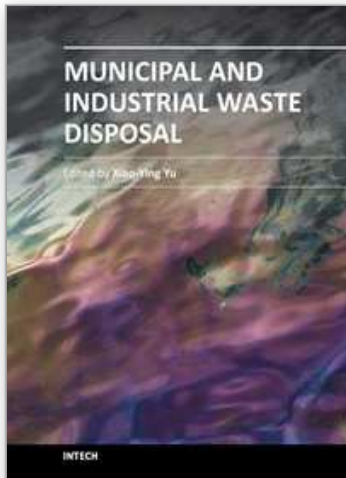
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Municipal and Industrial Waste Disposal

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This book reports research findings on several interesting topics in waste disposal including geophysical methods in site studies, municipal solid waste disposal site investigation, integrated study of contamination flow path at a waste disposal site, nuclear waste disposal, case studies of disposal of municipal wastes in different environments and locations, and emissions related to waste disposal.

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